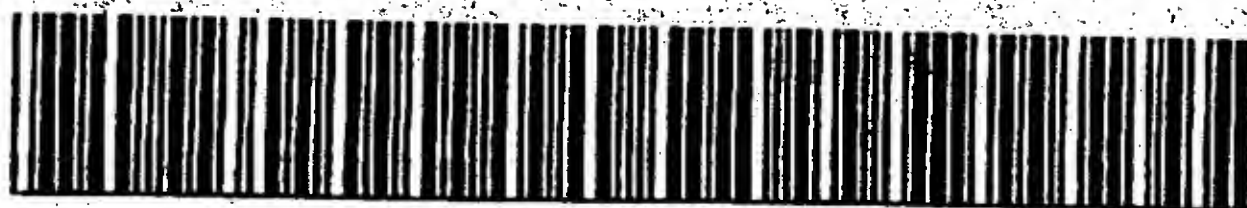


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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :

A01N 47/36, 43/653

A1

(11) International Publication Number:

WO 96/03878

(43) International Publication Date:

15 February 1996 (15.02.96)

(21) International Application Number: PCT/US95/08970

(22) International Filing Date: 21 July 1995 (21.07.95)

(30) Priority Data:

08/284,774

2 August 1994 (02.08.94)

US

(60) Parent Application or Grant

(63) Related by Continuation

US

Filed on

08/284,774 (CIP)

2 August 1994 (02.08.94)

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Company, Legal/Patent Records Center, 1007 Market Street,  
Wilmington, DE 19898 (US).(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ,  
EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT,  
LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI,  
SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT,  
BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL,  
PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN,  
ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD,  
SZ, UG).

Published

With international search report.

(54) Title: HERBICIDAL MIXTURES

(57) Abstract

This invention relates to herbicidal mixtures of methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridine-carboxylate and agriculturally suitable salts thereof with ethyl  $\alpha$ ,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate, herbicidal compositions of said mixtures, and a method for the use of said mixtures to control undesired vegetation.

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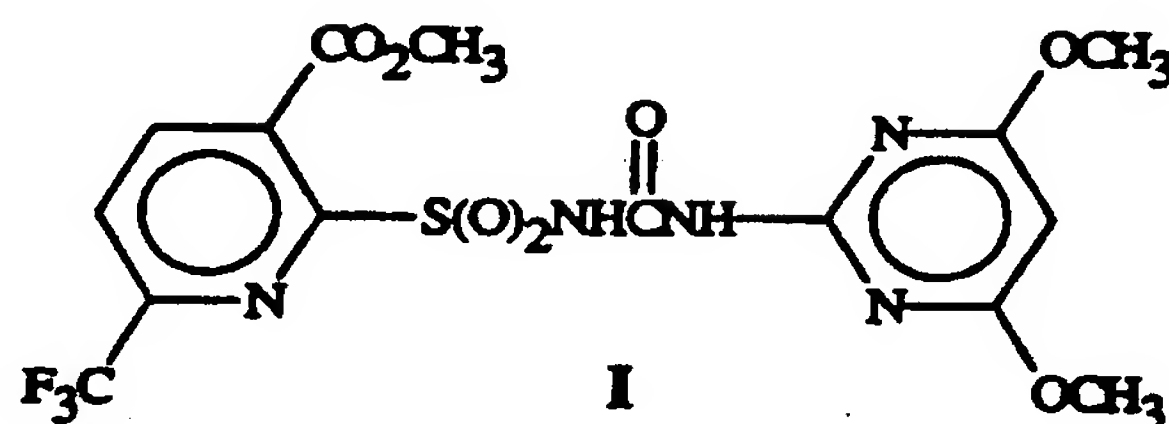
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GA	Gabon				

TITLEHERBICIDAL MIXTURESBACKGROUND OF THE INVENTION

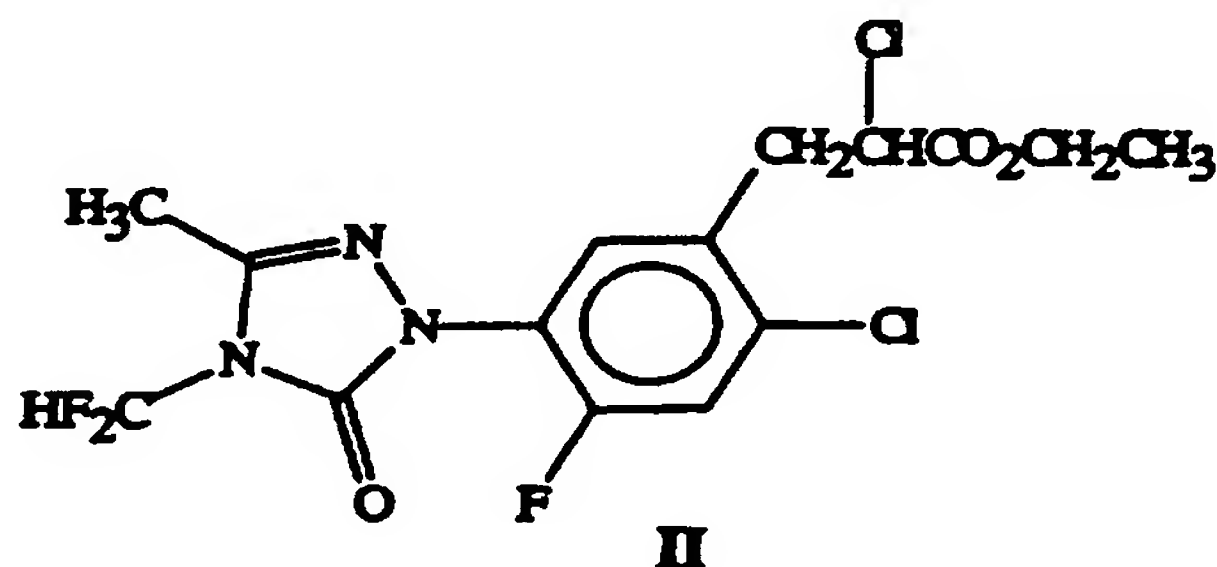
WO 94/09629 discloses mixtures of sulfonylureas and triazolinones, but does  
 5 not disclose the mixtures of this invention. WO 92/15576 and WO 90/02120  
 disclose Formula I compounds and the Formula II compound, respectively, but do  
 not disclose the mixtures of this invention.

SUMMARY OF THE INVENTION

This invention relates to mixtures of the sulfonylurea of Formula I

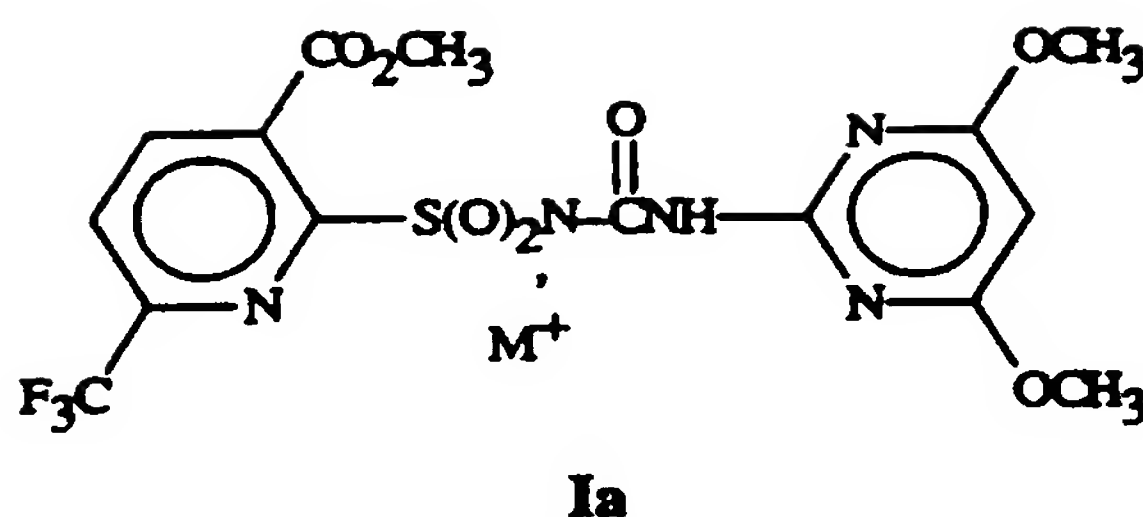


(methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-  
 (trifluoromethyl)-3-pyridinecarboxylate) and agriculturally suitable salts thereof  
 15 with the triazolinone of Formula II



(ethyl α,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-  
 20 triazol-1-yl]-4-fluorobenzenepropanoate), which have now been discovered to  
 synergistically control weeds. This invention also relates to herbicidal  
 compositions comprising effective amounts of the aforesaid mixtures and at least  
 one of the following: surfactant, solid or liquid diluent. This invention also relates  
 to a method for controlling undesired vegetation comprising applying to the locus  
 25 of the vegetation herbicidally effective amounts of the aforesaid mixtures.

Agriculturally suitable salts of the sulfonylurea of Formula I include, but are  
 not limited to, quaternary amine salts, and the alkali metal salts of Formula Ia



wherein M is an alkali metal, such as lithium, sodium or potassium.

The Formula II compound may exist as two stereoisomers which include the R- and S-enantiomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit other beneficial effects when enriched relative to the other stereoisomer or when separated from the other stereoisomer. One skilled in the art knows how to separate said enantiomers. Accordingly, the present invention comprises mixtures of Formula I sulfonylurea in admixture with the racemic mixtures, individual stereoisomers, and enriched optically active mixtures of the Formula II enantiomers.

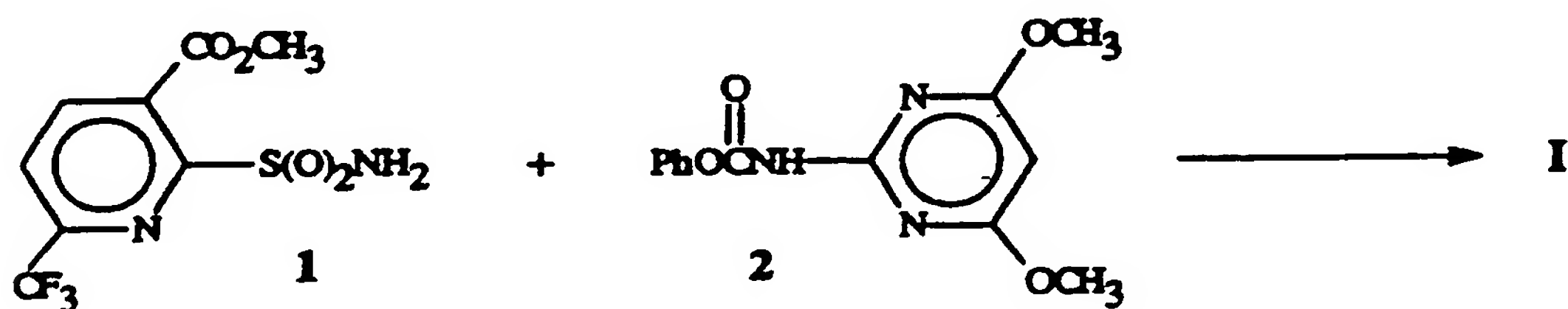
The mixtures of the invention preferred for enhanced activity include:

1. A herbicidal mixture comprising the sulfonylurea salt of Formula Ia wherein M is Na and the triazolinone of Formula II.
2. A herbicidal mixture comprising the sulfonylurea of Formula I and the triazolinone of Formula II.

For reason of weed control spectrum and/or crop selectivity, the preferred crops for application of the mixtures of this invention are wheat and barley.

#### DETAILS OF THE INVENTION

The Formula I sulfonylurea can be prepared as described in WO 92/15576. The synthesis involves the coupling of the pyridinesulfonamide of Formula 1 with the heterocyclic carbamate of Formula 2.



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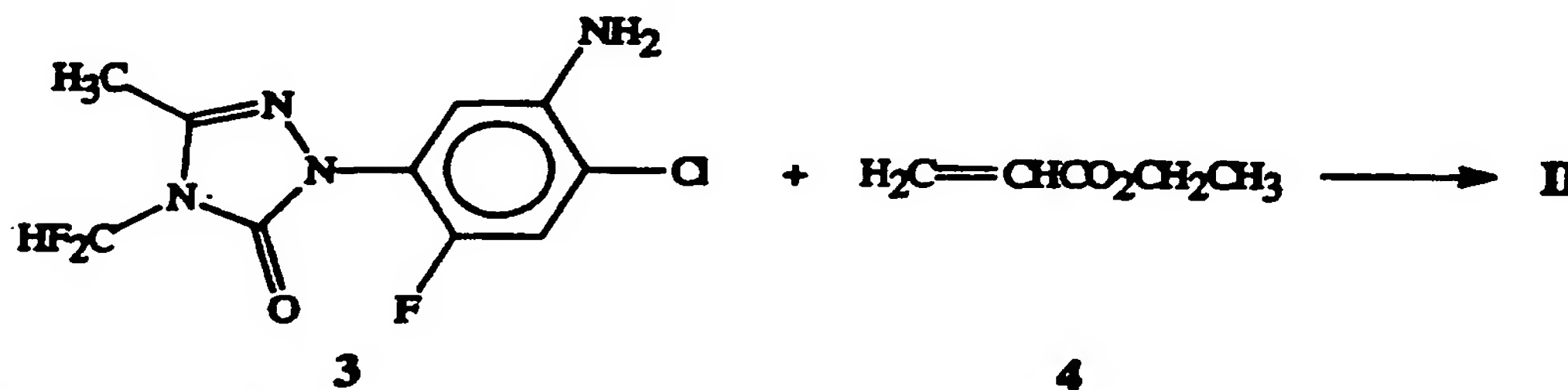
The mixtures of the present invention can include the sulfonylurea of Formula I as one or more of its agriculturally suitable salts. These can be prepared in a number of ways known in the art. For example, metal salts can be made by contacting the sulfonylurea of Formula I with a solution of an alkali or alkaline earth metal salt having a sufficiently basic anion (e.g., hydroxide, alkoxide,

carbonate or hydride). Quaternary amine salts can be made by similar techniques. WO 92/15576 describes the preparation of the salt of Formula Ia wherein M is Na by use of sodium methoxide.

Salts of the sulfonylurea of Formula I can also be prepared by exchange of one cation for another. Cationic exchange can be effected by direct contact of an aqueous solution of a salt of the sulfonylurea of Formula I (e.g., alkali or quaternary amine salt) with a solution containing the cation to be exchanged. This method is most effective when the desired salt containing the exchanged cation is insoluble in water and can be separated by filtration.

Exchange may also be effected by passing an aqueous solution of a salt of the sulfonylurea of Formula I (e.g., an alkali metal or quaternary amine salt) through a column packed with a cation-exchange resin containing the cation to be exchanged for that of the original salt and the desired product is eluted from the column. This method is particularly useful when the desired salt is water soluble (e.g., a potassium, sodium or calcium salt).

The Formula II triazolinone can be prepared by methods described in WO 90/02120 which involve the reaction of the aniline of Formula 3 with the acrylate of Formula 4 under Meerwein conditions.



### Formulation/Utility

The mixtures of the Formula I (including Formula Ia) and Formula II compounds can be formulated in a number of ways:

- (a) the Formula I and Formula II compounds can be formulated separately and applied separately or applied simultaneously in an appropriate weight ratio, e.g., as a tank mix; or
- (b) the Formula I and Formula II compounds can be formulated together in the proper weight ratio.

Mixtures of the Formula I and Formula II compounds will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent and/or a surfactant wherein the formulation is consistent with the physical properties of the active ingredients, mode of application and environmental factors such as soil type, moisture and temperature. Useful formulations include liquids



such as solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful formulations further include solids such as dusts, powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wettable") or water-soluble. Active ingredients can be (micro)-encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredients. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further formulation.

The formulations will typically contain effective amounts of active ingredients, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

15

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Water-Dispersible and Water-soluble Granules, Tablets and Powders	5-90	0-94	1-15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

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Surfactants include, for example, polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and

polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar, silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, 5 *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkyl naphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut, cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, 10 cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Chemically stabilized aqueous sulfonylurea or agriculturally suitable sulfonylurea salt dispersions are taught in U.S. 4,936,900. Solution formulations of sulfonylureas with improved chemical stability are taught 15 in U.S. 4,599,412. Dusts and powders can be prepared by blending and, usually, grinding as in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical* 20 *Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as 25 taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in GB 2,095,558 and U.S. 3,299,566.

For further information regarding formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 30 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations 35 are prepared in conventional ways. Compound numbers refer to compounds identified on Page 8.

Example AHigh Strength Concentrate

	Compound 1	33.0%
	Compound 2	65.5%
5	silica aerogel	0.5%
	synthetic amorphous fine silica	1.0%.

Example BWettable Powder

	Compound 1	22.0%
10	Compound 2	43.0%
	dodecylphenol polyethylene glycol ether	2.0%
	sodium ligninsulfonate	4.0%
	sodium silicoaluminate	6.0%
	montmorillonite (calcined)	23.0%.

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Example CGranule

	Compound 1	3.5%
	Compound 2	6.5%
20	attapulgit granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example DAqueous Suspension

	Compound 1	8.5%
	Compound 2	16.5%
25	hydrated attapulgit	3.0%
	crude calcium ligninsulfonate	10.0%
	sodium dihydrogen phosphate	0.5%
	water	61.5%.

Example E30 Extruded Pellet

	Compound 1	8.5%
	Compound 2	16.5%
	anhydrous sodium sulfate	10.0%
	crude calcium ligninsulfonate	5.0%
35	sodium alkyl naphthalenesulfonate	1.0%
	calcium/magnesium bentonite	59.0%.

Test results indicate that mixtures of compounds of Formula I and Formula II are highly active herbicides, providing unexpected synergistic control of

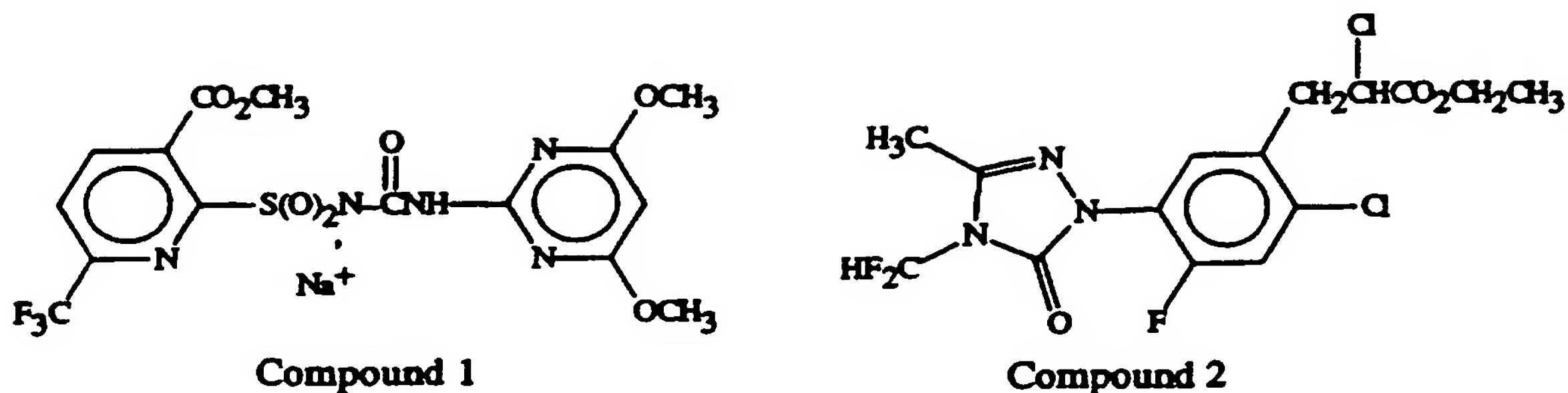


selected grass and broadleaf weeds. The mixtures are valued, because they retain acceptable levels of crop selectivity in certain major agronomic crops such as barley, cotton, wheat, corn, soybeans and rice. The mixtures are particularly valued because of the acceptable levels of crop selectivity they retain in barley and wheat.

The Formula I and Formula II mixtures of this invention can additionally be used in combination with other commercial herbicides, insecticides or fungicides. A mixture of one or more additional herbicides with the Formula I and Formula II mixtures of this invention may be particularly useful for weed control. Examples of other herbicides as mixture partners are: anilofos, bensulfuron methyl, chlorsulfuron, cinosulfuron, imazamethabenz, mefluidide, metsulfuron methyl, rimsulfuron, thifensulfuron methyl, triasulfuron and tribenuron methyl, and herbicides with a similar spectrum of control but a different mode of action such as, but not limited to: barban, bentazon, bifenox, bromoxynil, bromoxynil heptanoate, bromoxynil octanoate, chloridazon, chlortoluron, clodinafop, clopyralid, cyanazine, dicamba, diclofop, dichlorprop, diclofop, difenzoquat, fenoxaprop, flamprop, flupoxam, fluridone, flurtamone, glufosinate, glyphosate, ioxynil, isoproturon, isoxaben, MCPA, MCPA-thioethyl, MCPB, mecoprop, mecoprop-P, methabenzthiazuron, metribuzin, pendimethalin, tri-allate, tralkoxydim, trifluralin, (2,4-dichlorophenoxy)acetic acid, and 4-(2,4-dichlorophenoxy)butanoic acid. In certain instances, combinations with herbicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

An herbicidally effective amount of both the compounds of Formula I and Formula II will vary depending on the specific compounds selected, environmental conditions, formulation, method of application, amount and type of vegetation present, etc. The use rate ratios of Formula I to Formula II are in general 1:15 to 1:1, with ratios of 1:4 to 1:1 preferred for most uses. A use rate ratio of 1:2 is particularly preferred. In general, the Formula I compounds should be applied at a rate from 0.0005 to 1 kg ai/ha and Formula II compounds should be applied at a rate from 0.001 to 2 kg ai/ha. Preferably, Formula I compounds should be applied at a rate from 0.002 to 0.03 kg ai/ha, and the Formula II compound should be applied at a rate from 0.004 to 0.03 kg ai/ha. One skilled in the art can readily determine application rates and ratios of herbicides of Formula I to the herbicide of Formula II as well as timing necessary for the desired level of weed control and crop safety.

The following Formula I sulfonylurea (Compound 1) was tested in combination with the Formula II triazolinone (Compound 2).



The following Test protocol was used for the Tests in Tables 1-3. The data demonstrate the efficacy of the Formula I and Formula II mixtures of this invention against specific weeds. The weed control afforded by the mixtures of this invention are not limited, however, to these species.

#### Test Protocol

Cereal crops were planted during fall into areas of high natural infestations of weed species such as; *Galium aparine* (GALAP), *Viola arvensis* (VIOAR), and various *Veronica sp.* (*V. persica* (VERPE), and *V. hederifolia* (VERHE)). Test plots were typically 20 sq meters (2 meters wide by 10 meters in length), with the entire test plot area treated postemergence to the crops and weeds. Compound 1 and Compound 2 were both formulated as single active ingredients in 50% strength dry flowable granules. Compound 1 and Compound 2 were formulated as a mixture in a ratio of 1:2 respectively, in 50% total active ingredient strength paste extruded granules. Herbicides were applied to the test area by diluting the formulated herbicides in an aqueous solution to the appropriate concentration to deliver the desired use rate, spray volumes between 150 to 300 L/ha were typically used. The prepared test solutions were then sprayed onto the test plot using approximately 2 bars pressure through standard T-Jet flat-fan nozzles. Unless specifically indicated, no additional adjuvants such as surfactants were added to the spray solution. Individual treatments were typically replicated three times at any given field trial location.

Assessments of weed control were made by visual inspection at intervals following herbicide application. The specific tests for Tables 1-3 were final evaluations which ranged from 34 to 200 days after application. A visual rating system was used based on a percentage scale from 0 to 100%, relative to an adjacent untreated control plot or test area. On this scale 0% represents no visual differences relative to an untreated control, 100% represents complete kill of the given crop or weed species.

Colby's equation was used to calculate the expected additive herbicidal effect of the mixtures of Compound 1 and Compound 2. Colby's equation (Colby, S. R.

"Calculating Synergistic and Antagonistic Responses of Herbicide Combinations," *Weeds*, 15(1), pp 20-22 (1967)) calculates the expected additive effect of herbicidal mixtures, and for two active ingredients is of the form:

$$P_{a+b} = P_a + P_b - (P_a P_b / 100)$$

- wherein  $P_{a+b}$  is the percentage effect of the mixture expected from additive contribution of the individual components,  
 $P_a$  is the observed percentage effect of the first active ingredient at the same use rate as in the mixture, and  
 $P_b$  is the observed percentage effect of the second active ingredient at the same use rate as in the mixture.

Tables 1 through 3 represent final visual assessments of control of specific weeds with Compound 1 and Compound 2 applied alone as single active ingredients, applied as a mixture of the two active ingredients of Compound 1 and Compound 2, and the expected additive effect of the herbicidal mixture of Compound 1 and Compound 2 (Colby's equation). Different ratios of Compound 1 to Compound 2, and different formulation types, should also provide useful weed control from the combination of the two herbicides.

**TABLE 1\***

Control of *Viola arvensis* Using Compound 1 and Compound 2  
as Single Active Ingredients and in Admixture

Compound	Rate (g ai/ha)	Test 1	Test 2	Test 3	Test 4	Test 5
1	10	72	38	0	35	75
2	20	83	63	0	10	50
1 + 2	10 + 20	97 (95)†	97 (77)	65 (0)	70 (42)	100 (88)

\* Tests 1-5 were conducted at different locations. Data are reported as percent control

† Expected effects in parentheses are calculated according to Colby, S. R. "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations," *Weeds*, 15(1), pp 20-22 (1967)

**TABLE 2\***

Control of Two *Veronica* sp. Using Compound 1 and Compound 2 as  
Single Active Ingredients and in Admixture

Compound	Rate (g ai/ha)	VERPE†			VERHE†		
		Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
1	10	37	47	0	0	20	23
2	20	100	92	50	70	70	89
1 + 2	10 + 20	100 (100)‡	98 (96)	70 (50)	80 (70)	85 (76)	97 (92)

\* Tests 1–6 were conducted at different sites. Data are reported as percent control

† Weed species: VERPE = *Veronica persica*; VERHE = *Veronica hederaefolia*

‡ Expected effects in parentheses are calculated according to Colby, S. R. "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations," *Weeds*, 15(1), pp 20–22 (1967)

**TABLE 3\***

Control of *Galium aparine* Using Compound 1 and Compound 2  
as Single Active Ingredients and in Admixture

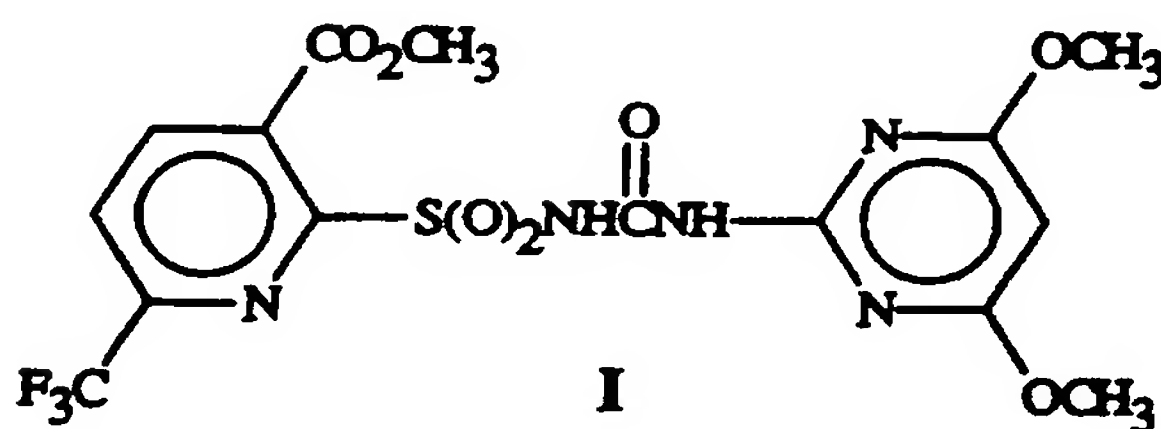
Compound	Rate (g ai/ha)	Test 1	Test 2	Test 3	Test 4
1	10	70	85	55	75
2	20	89	90	75	85
1 + 2	10 + 20	94 (97)†	100 (98)	90 (89)	99 (96)

\* Tests 1–4 were conducted at different sites. Data are reported as percent control

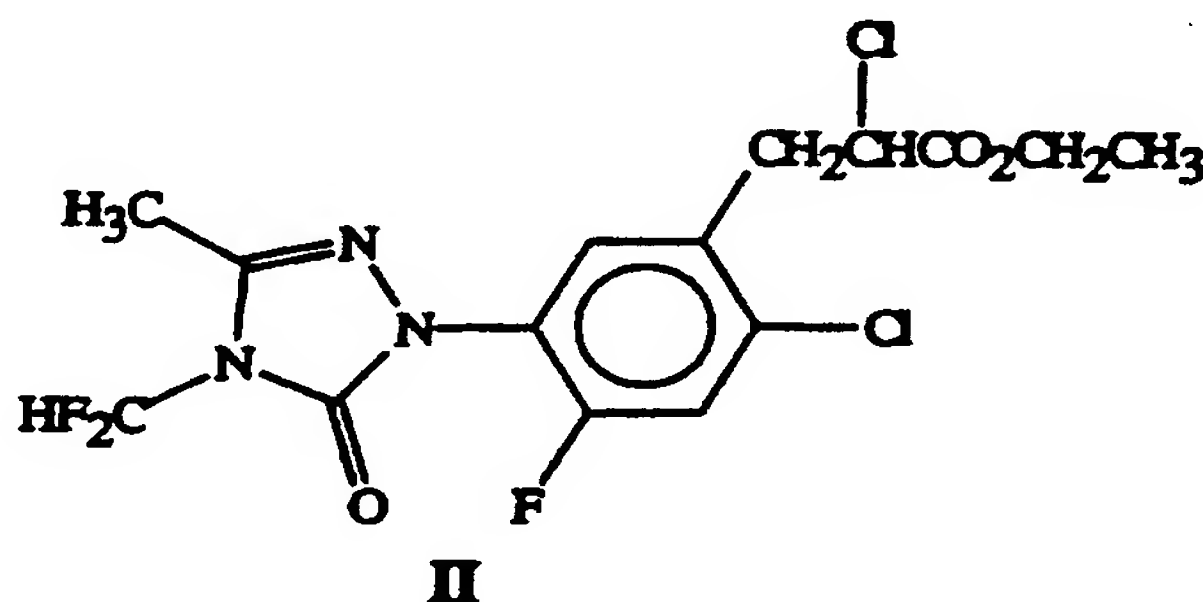
† Expected effects in parentheses are calculated according to Colby, S. R. "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations," *Weeds*, 15(1), pp 20–22 (1967)

CLAIMS

1. A herbicidal mixture comprising an herbicidally effective amount of the compound of Formula I



which is methyl 2-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]-sulfonyl]-6-(trifluoromethyl)-3-pyridinecarboxylate and agriculturally suitable salts thereof and an herbicidally effective amount of the compound of Formula II



which is ethyl  $\alpha$ ,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate.

2. An agriculturally suitable composition for controlling the growth of undesired vegetation comprising an effective amount of the herbicidal mixture of Claim 1 and at least one of the following: surfactant, solid or liquid diluent.

3. A method for controlling the growth of undesired vegetation comprising contacting the locus to be protected with a herbicidally effective amount of the composition of Claim 2.

4. A herbicidal mixture of Claim 1 comprising the sodium salt of the compound of Formula I and the compound of Formula II.



# INTERNATIONAL SEARCH REPORT

International application No.

PC., US 95/08970

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: A01N 47/36, A01N 43/653

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS, WPI, USPATFULL, CAB ABSTRACT, BIOSIS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A1, 9409629 (FMC CORPORATION), 11 May 1994 (11.05.94), claims 2,9-11,13,20-22 --	1-4
A	WO, A1, 9215576 (E.I. DU PONT DE NEMOURS AND COMPANY), 17 Sept 1992 (17.09.92) --	1-4
A	WO, A1, 9002120 (FMC CORPORATION), 8 March 1990 (08.03.90) -- -----	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

24 October 1995

Date of mailing of the international search report

17. 11. 95

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Gerd Strandell

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

PCT/US 95/08970

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9409629	11/05/94	NONE	
WO-A1- 9215576	17/09/92	AU-B- 655255	08/12/94
		AU-A- 1545792	06/10/92
		BG-A- 98094	30/06/94
		BR-A- 9205735	08/11/94
		CZ-A- 9301832	16/03/94
		EP-A- 0502740	09/09/92
		EP-A- 0575503	29/12/93
		HU-A- 65438	28/06/94
		HU-D- 9302530	00/00/00
		JP-T- 6505489	23/06/94
		US-A- 5393734	28/02/95
WO-A1- 9002120	08/03/90	AU-B,B- 626324	30/07/92
		AU-A- 4210489	23/03/90
		CA-A- 1331463	16/08/94
		EG-A- 18737	30/12/93
		EP-A,B- 0432212	19/06/91
		IL-A- 91416	25/01/94
		JP-T- 3503053	11/07/91
		JP-B- 5015708	02/03/93
		OA-A- 9638	30/04/93
		PL-B- 161816	31/08/93
		US-A- 5125958	30/06/92
		US-A- 5208212	04/05/93
		US-A- 5217520	08/06/93

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